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AUTOIGNITION OF DOWTHERM A IN AIR AT ELEVATED PRESSURES

FINAL REPORT NO. 3905
June 3 to November 30, 1963

BUREAU OF MINES, PITTSBURGH, PA.

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By

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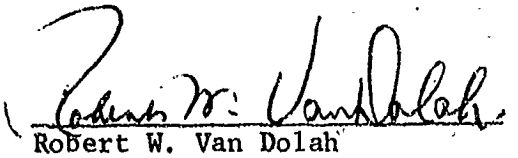
APPROVED:



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INTRODUCTION

A number of heat transfer fluids are currently available for use at elevated temperatures.[1/] Each has certain desirable and undesirable properties and related characteristics (thermal stability, fire resistance, vapor pressure, toxicity, corrosiveness, cost, lubricity, etc.). In general, these properties are considered under the conditions of fluid use. For example, where the hot fluid may contact an oxidizing atmosphere at elevated pressures, one must determine the resultant hazards at such pressures. In the present study, the autoignition temperature of Dowtherm A (a eutectic mixture of diphenyl and diphenyl oxide)[2/] was determined in air at pressures between 0 and 1500 psig. All determinations were made in the Bureau of Mines elevated pressure apparatus.[3/]

RESULTS AND DISCUSSION

A summary of the minimum autoignition temperatures (AIT) of Dowtherm A over the pressure range 0 to 1500 psig (1 to 103 atmospheres) is given in the following table:

1/ Uhl, V. W., and H. P. Voznick, "Molten Salt as a Heat Transfer Medium". Chem. Eng. Prog., v. 59, pp. 33-35, 1963.
Peterson, D. E., and R. K. Bedell, "UCON Heat Transfer Fluid," ibid, pp. 36-39.
Davis, W. J., and P. G. Benignus, P. G., "Therminol FR-2 Heat Transfer Systems," ibid, pp. 39-42.
Purdy, R. B., R. Balow, J. J. Shaffer, and J. P. Fanaritis, "Indirect Heating with Aromatic Oils," ibid, pp. 43-46.
Conant, A. R., and W. F. Seifert, "Dowtherm Heat Transfer Medium," ibid, pp. 46-49.
Geiringer, P. L., and E. Beanland, "Silicon Compounds as Heat Transfer Media," ibid, pp. 50-53.

2/ Composition: 26.5% diphenyl and 73.5% diphenyl oxide.

3/ Zabetakis, Michael G., George S. Scott, and Robert E. Kennedy, "Autoignition of Lubricants at Elevated Pressures". BuMines Rept. of Investigations 6112, 1962.

Initial Pressure (psig)	(atm)	AIT (°C)	(°F)	τ (sec)
0	1.0	610	1130	15
25	2.7	568	1054	42
50	4.4	522	972	77
150	11.2	490	914	102
220	16.0	480	896	123
400	28.2	447	837	1
600	41.6	390	734	49
800	55.4	330	626	37
1500	103	295	563	1

The last column lists the observed time delay before ignition (τ) at the AIT value; in general, τ decreases as the bomb temperature increases above the AIT value at each pressure. The fluid injection pressure also affects the value of τ and, to a lesser extent, the AIT value obtained at a particular pressure. The values recorded here are the lowest obtained with new fluid; slightly higher values (5 to 10 C°) were obtained with used fluid.

The autoignition data obtained at an initial pressure of 16 atmospheres (220 psig) are typical of the results obtained in this study. These are presented in Figures 1 and 2 for a range of fluid volumes between 0.2 and 3.0 cc with both new and used fluid. The sample regression line of log τ on $10^3/T$ obtained by the method of least squares is

$$\log \tau = -7.05 + 6.78 \left(\frac{10^3}{T}\right) \quad . \tag{1}$$

The standard error of estimate of log τ about the sample regression line is 0.089; parallel lines are constructed in Figure 2 at vertical distances of $\pm 2 \times 0.089$ units from the regression line (95% tolerance interval). This defines a band which includes all but 2 of the experimental points. This band and the sample regression line are also included in Figure 1.

Expressing equation 1 as[4/]

$$\log \tau = \frac{0.22E}{T} + \text{constant}, \tag{2}$$

the apparent activation energy, E, is 31 Kcal for the ignition reaction at 16 atmospheres. This value (31 Kcal) compares favorably with the values obtained for many other hydrocarbons.

Unfortunately, the above equations give only the time delays before ignition for a range of temperatures at which ignition is known to occur. They do not give the lowest temperature at which ignition can

4/ Semenov, N. N., " Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, N. J., v. 2, 1959, p. 109.

occur in a particular system. In practice, this lowest temperature is obtained experimentally at each pressure of interest in a system that is large enough to minimize wall quenching. For example, from Figure 1, we see that 480° C is the lowest temperature at which ignition was obtained at 16 atmospheres. All trials at lower temperatures, and some at higher temperatures, resulted in ignition failures ("no-ignitions"). Preliminary experiments yielded a higher "lowest value" of the ignition temperature at a one second time delay. This value could not be repeated in subsequent trials so it was discarded and observations were then made over the temperature range 433° to 570° C.

Observations were made over a range of temperatures at each of nine pressures; a summary of the minimum autoignition temperature (AIT) obtained in each case is given above and presented graphically in Figure 3. The sample regression line of AIT on log P over the pressure interval 1 to about 30 atmospheres is

$$\text{AIT } (°C) = 608 - 111 \log P \qquad (3)$$

The standard error of estimate of AIT about the sample regression line is 9 C°. This estimate is used to define the 95% tolerance interval in Figure 3.

For the pressure interval 28 to 103 atmospheres, the linear regression line of AIT on log P is

$$\text{AIT } (°C) = 831 - 273 \log P \qquad (4)$$

In this case, the error of estimate of AIT about this linear sample regression line is 22 C°. In practice, AIT does not ordinarily vary linearly with log P at such elevated pressures [3] so that equation 4 should be considered a crude estimate at best. According to Semenov's theory,[4] a thermal reaction is characterized by a linear relationship between the logarithm of $P/T^{1+2/n}$ and $1/T$ where n is the order of the reaction. Such a plot is linear for both first and second order reactions only over the pressure range 1 to 30 atmospheres, so the nature of the preignition reaction must change at the higher pressures considered here.

CONCLUSIONS

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The above data are presented in the summary diagram given in Figure 4 which also gives the operating range of interest and the vapor pressure of Dowtherm A between 460 and 750° F. English units are used in this figure to simplify its use by engineering personnel. In brief, the

data given here indicate that autoignition of Dowtherm A should not occur in the normal operating range. However, an increase in the working temperature maximum at the specified pressure maximum (600 psia) should be considered hazardous; conversely, an increase in the working pressure at the specified temperature maximum (680° F) should also be considered hazardous with Dowtherm A. An increase in one variable (temperature or pressure) should be offset by a decrease in the other variable to prevent overlap of the operating range and the autoignition region.

Author

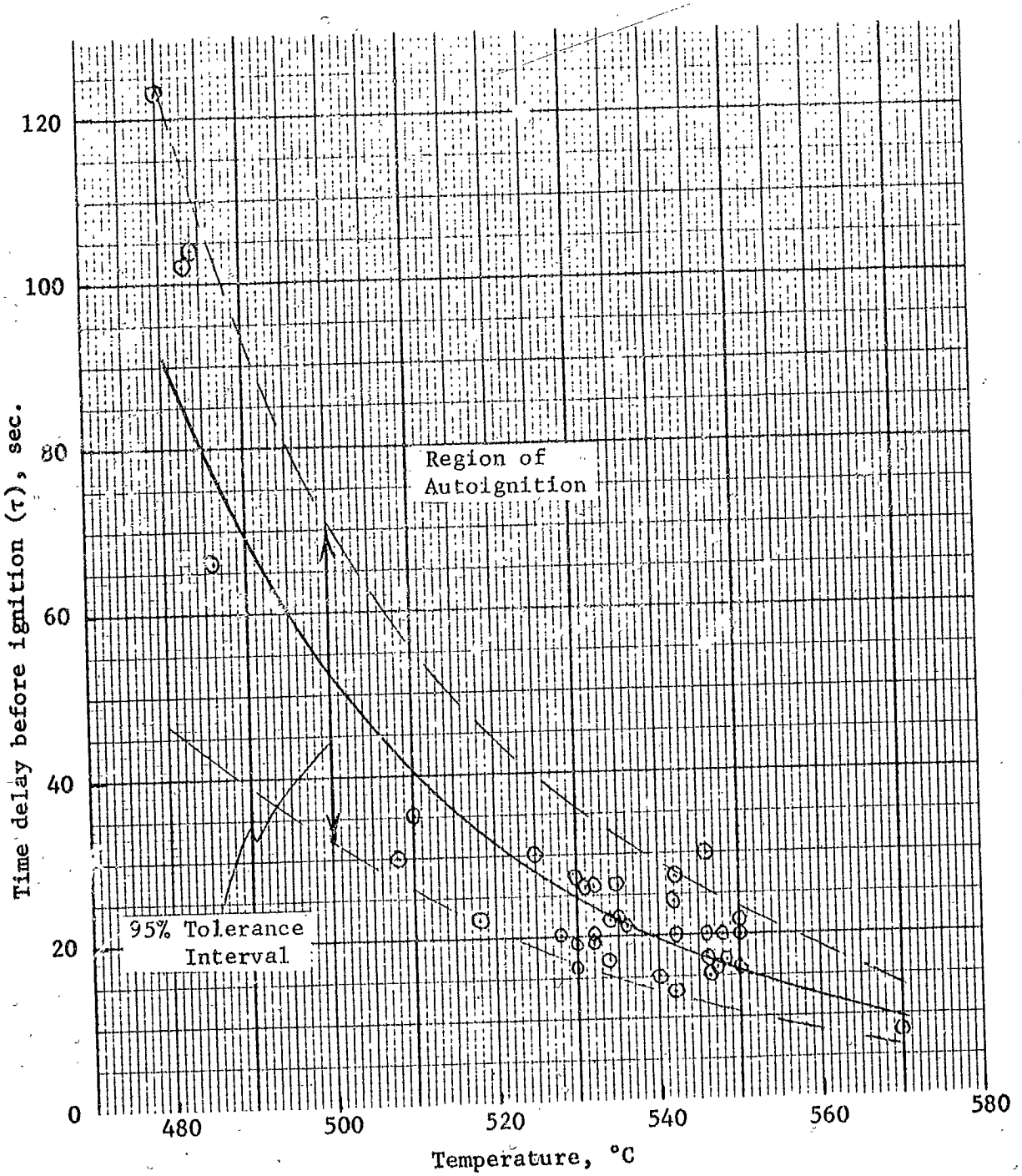

Figure 1. - Time delay before ignition of Dowtherm A in air for various temperatures at 16 atmospheres in a 450 cc cylindrical stainless steel bomb.

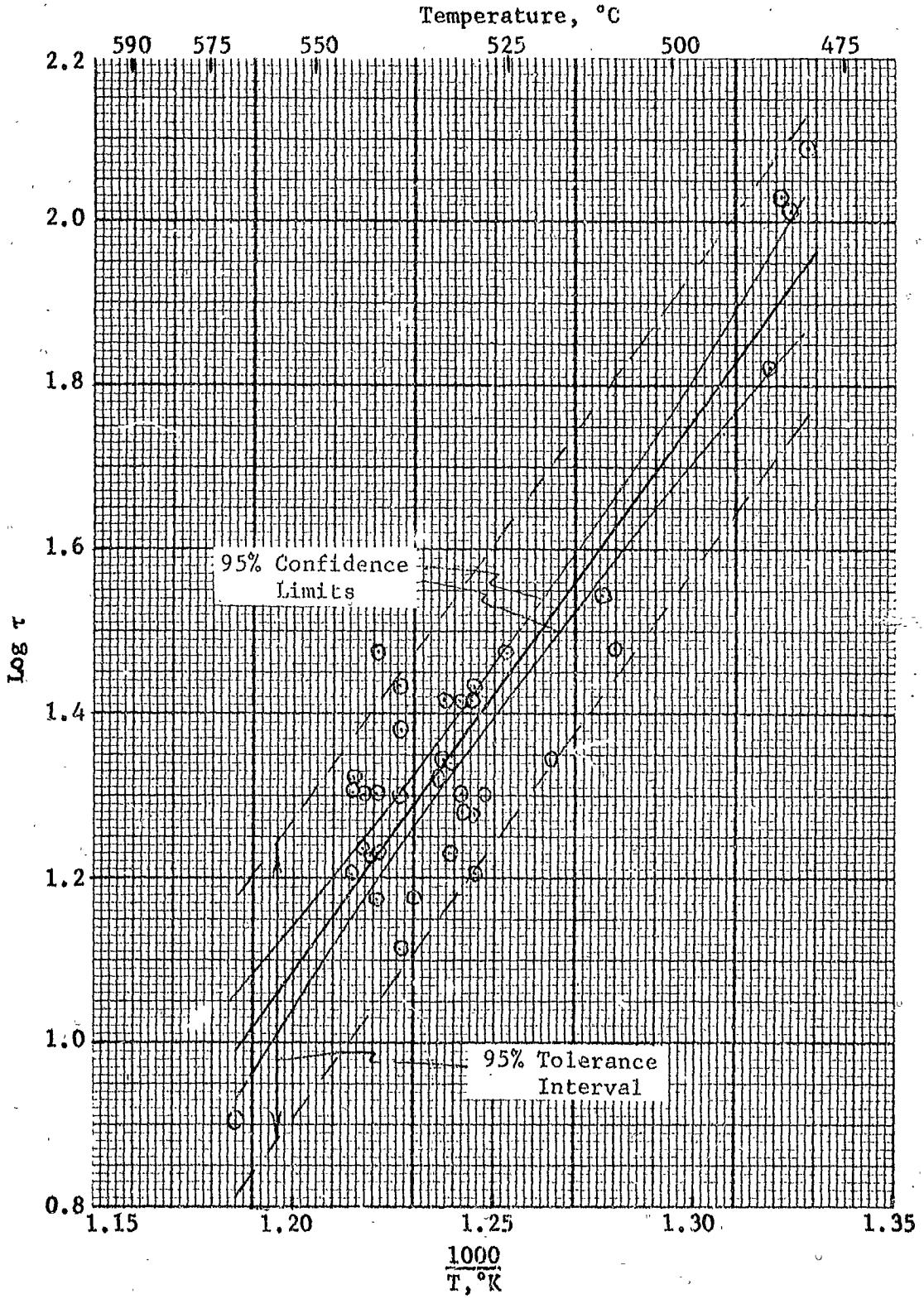

Figure 2. - Logarithm of the time delay before ignition of Dowtherm A in air for various reciprocal temperatures at 16 atmospheres. (Data from Figure 1).

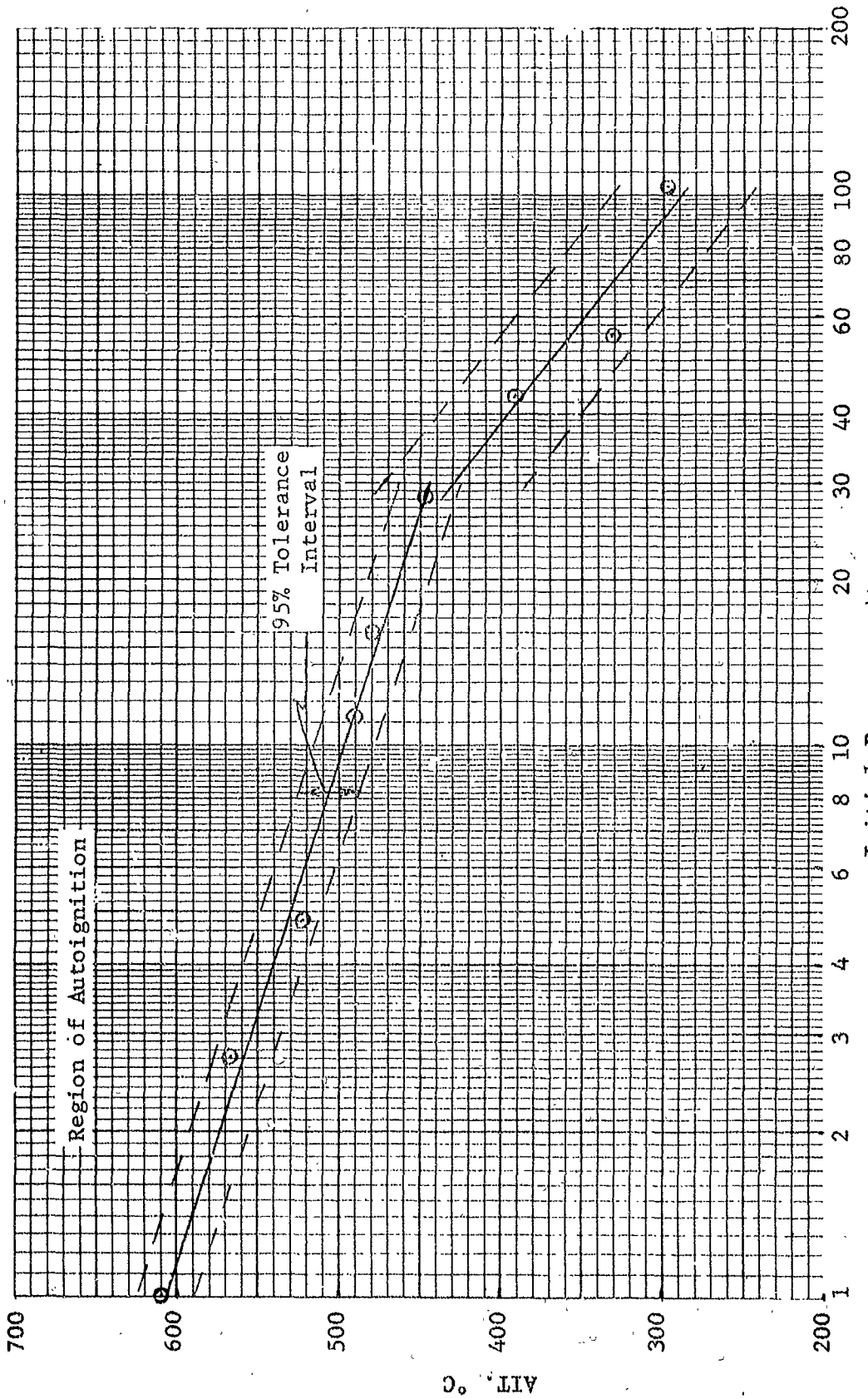

Figure 3. - Variation in minimum autoignition temperature with pressure of Dowtherm A in air in a 450 cc stainless steel bomb.

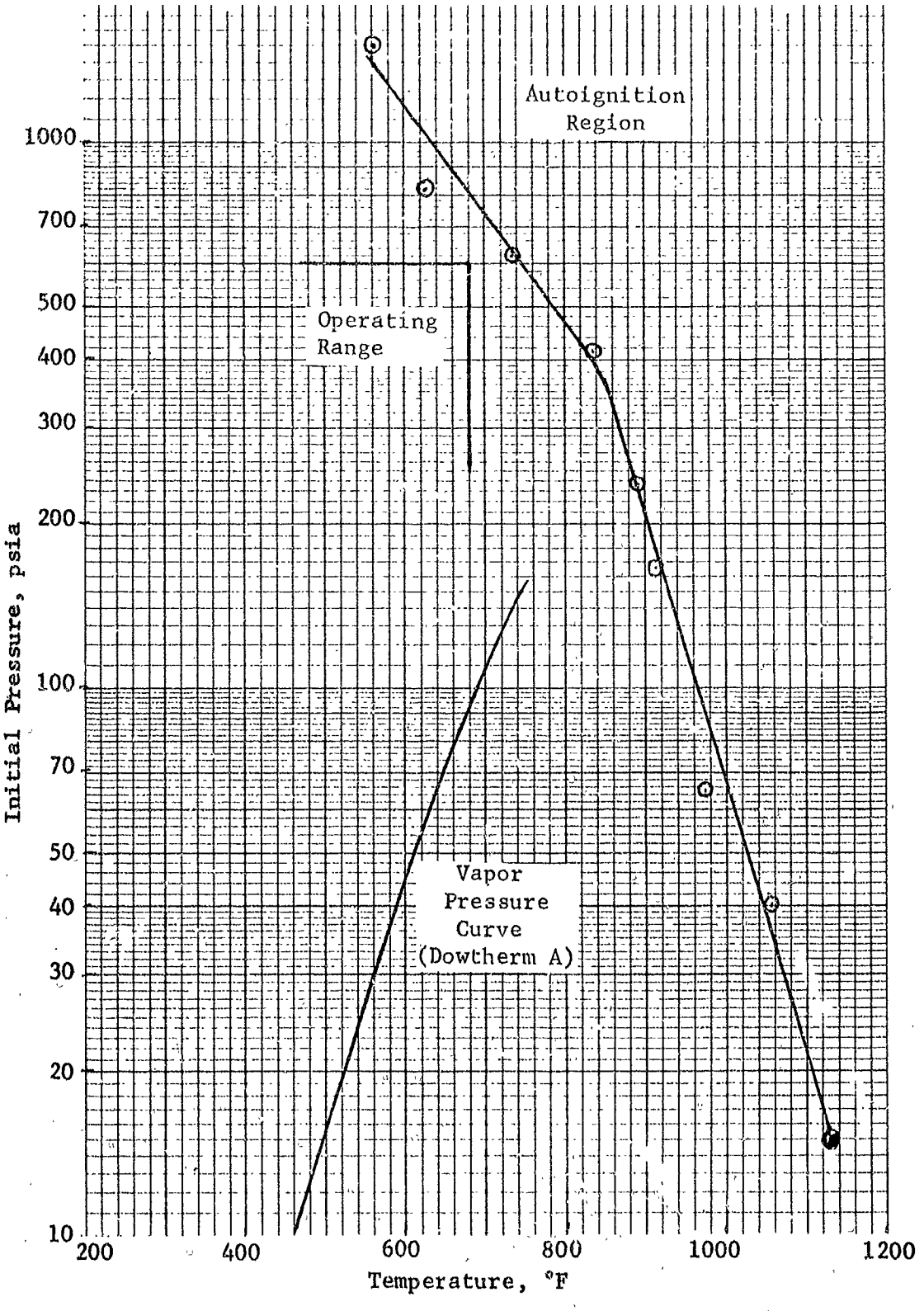

Figure 4. - Location of the autoignition region of Dowtherm A heat transfer fluid in air, the approximate air operating range, and the vapor pressure curve of Dowtherm A.

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